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A novel process for recovery of fermentation-derived succinic acid: Process design and economic analysis

Alvaro Orjuela [a,b], Andrea Orjuela [a,b], Carl T. Lira [a], Dennis J. Miller [a,*]

[a] Department of Chemical Engineering & Materials Science, Michigan State University, 2527 Engineering Building, East Lansing, MI 48824, United States
[b] Universidad Nacional de Colombia, Ciudad Universitaria, Depto. de Ingeniería Química y Ambiental, Bogotá, Colombia

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ABSTRACT

Recovery and purification of organic acids produced in fermentation constitutes a significant fraction of total production cost. In this paper, the design and economic analysis of a process to recover succinic acid (SA) via dissolution and acidification of succinate salts in ethanol, followed by reactive distillation to form succinate esters, is presented. Process simulation was performed for a range of plant capacities (13–55 million kg/yr SA) and SA fermentation titers (50–100 kg/m^3). Economics were evaluated for a recovery system installed within an existing fermentation facility producing succinate salts at a cost of $0.66/kg SA. For a SA processing capacity of 54.9 million kg/yr and a titer of 100 kg/m^3 SA, the model predicts a capital investment of $75 million and a net processing cost of $1.85 per kg SA. Required selling price of diethyl succinate for a 30% annual return on investment is $1.57 per kg.

1. Introduction

Fermentation-derived succinic acid (SA) is a valuable intermediate that can potentially replace maleic anhydride as a renewable building block for chemical commodities such as 1,4-butanediol (BDO), tetrahydrofuran (THF), γ-butyrolactone (GBL), polybutylene succinates (PBS), succinimides, and succinate salts among others. In total, SA has a potential market of around 1.6 million tonnes per year as a chemical platform (De Jong et al., 2012; Bechthold et al., 2008). However, the current price of petrochemical-derived maleic anhydride (~$1.75/kg) and its established infrastructure make it difficult for SA obtained by carbohydrate fermentation to compete in the present marketplace.

Even though cost is a primary concern for the commercial success of bio-based SA, it is recognized that the fermentation route to SA has a net fossil energy consumption of 30–40% less than the current petroleum-based route (Sauer et al., 2008). In addition, SA can be produced from a variety of feed stocks and microorganisms (Cheng et al., 2012; Kagliwal et al., 2013; Thakker et al., 2012; Wu et al., 2012) with net consumption of CO_2, making it possible to integrate its production into existing ethanol biorefineries. These positive attributes have been recognized by several companies who are working to commercialize bio-based SA production; currently several demonstration plants are under construction or in operation (De Jong et al., 2012).

In general for bio-based SA or other carboxylic acid production, 50% to 60% of processing costs are attributed to recovery and refining to obtain the final product (Kurzrock and Weuster-Botz, 2010). Major challenges in SA recovery are the relatively low titers in fermentation (50–100 kg/m^3), production of SA in salt form because pH control is required during fermentation, and the formation of byproducts. Acetic acid (AcA) has been reported to be the major byproduct (5–40 kg/m^3) in SA fermentation (Agarwal et al., 2005; Song and Lee, 2006) and is examined here, although other carboxylic acids can be formed.

To overcome these challenges, several methods have been proposed to recover SA from fermentation (Kurzrock and Weuster-Botz, 2010; McKinlay et al., 2007). After acidification of the broth to release SA in aqueous solution, selective precipitation (Berglund, 1991; Collins et al., 2003), extraction with solvents and/or amines (Holtzapple et al., 2002), ion exchange (Cockrem et al., 2003), membrane separation (Glassner and Datta, 1992) and even esterification (Bauduin et al., 2009; Dunuwila, 2009) have been reported. Among these, esterification is of special interest for production of commodities such as tetrahydrofuran and 1-4 butanediol (Varadarajan and Miller, 1999), as succinate ester can readily replace maleic anhydride as a feed for these products because it is an intermediate in their production. Thus, succinate recovery as esters directly from fermentation broth is of economic interest.

Recent research in our laboratory has demonstrated that SA in salt form can be recovered from fermentation by drying, followed by dissolution in acidified ethanol (EtOH) where free SA is liberated and partially esterified (Orjuela et al., 2012a). The

* Corresponding author. Tel.: +1 (517) 353 3928.
E-mail address: millerd@egr.msu.edu (D.J. Miller).

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partially-esterified SA solution in ethanol is then further converted to the desired diethyl succinate product by reactive distillation.

Reactive distillation (RD) is well suited for thermodynamically limited reactions such as esterification, because continuous product removal via distillation can drive the reaction to completion. Reactive distillation has been examined for numerous chemical processes, some of which have been implemented at the industrial scale (Hiwale et al., 2004; Jam Harmsen, 2007). In this direction, we have applied RD to esterify SA and AcA mixtures to simultaneously remove water (H_2O), separate diethyl succinate (DES) from ethyl acetate (EtAc), and recover pure DES in a single column (Orjuela et al., 2012b, 2011a).

In this work, a detailed design for the SA recovery process we have developed is described using Aspen Plus® process simulation software (Version 7.2, AspenTech). An economic evaluation is presented that includes major cost components such as raw materials, capital equipment, utilities, labor, and other economic factors.

2. Process description

2.1. Process concept

The full experimental development of the SA recovery process from fermentation is presented elsewhere (Orjuela et al., 2011a,b, 2012a,b). The process concept involves concentrating fermentation broth and partial drying, dissolution of dried succinate salts into EtOH, acidification with sulfuric acid (H_2SO_4), and partial esterification in a stirred reactor, followed by reactive distillation of the resulting mixture to produce a pure diethyl succinate product. The acidification of sodium salts of succinic acid and acetic acid in ethanol is represented in Eqs. (1) and (2), where it is seen that sodium sulfate precipitates upon addition of H_2SO_4.

$$Na_2Suc\ (s) + H_2SO_4\ (l) \rightarrow SA\ (sol) + Na_2SO_4\ (s) \quad (1)$$

$$2\,NaAc\ (s) + H_2SO_4\ (l) \rightarrow 2\,AcA\ (sol) + Na_2SO_4\ (s) \quad (2)$$

Esterification of SA to DES occurs in series reactions with monoethyl succinate (MES) as an intermediate product. Formation of diethyl ether (DEE) from EtOH is also considered in the reaction system.

A block diagram of the process is presented in Fig. S1 of the Supplementary information (Orjuela et al., 2011b). In a first section of the process, the fermentation broth is treated by typical centrifugation or filtration to remove cell biomass and by clarification to remove impurities and color. Water is then removed by evaporation until the succinate and acetate salts precipitate. Wet salt solids can be recovered by filtration. If calcium or magnesium are used as neutralizing cations, complete evaporation of water is not required because the succinate salts formed have low solubility in water and thus precipitate.

In the second section, the acid salts are dissolved into EtOH along with H_2SO_4 as the acidulant. In general, a modest excess (5–20%) of H_2SO_4 is used to ensure complete acidification and to provide acid catalyst for esterification. The free SA and AcA dissolve into ethanol and partially esterify as they dissolve. The quantity of EtOH used can be adjusted in order to dissolve all SA present at the temperature of dissolution. The resulting inorganic sulfate (herein Na_2SO_4) is virtually insoluble in EtOH, and thus precipitates and is removed by centrifugation or filtration. The inorganic sulfate may form a hydrate, enhancing the removal of water from the system as esterification proceeds.

In the third section, the partially esterified mixture is sent to a RD column where high purity DES is obtained as bottom product. Ethyl acetate is recovered in the distillate stream along with excess EtOH and H_2O. Recovery of pure EtAc and recycle of excess EtOH requires additional separation steps for the distillate stream.

2.2. Detailed description

The process flow diagram for production of DES is presented in Fig. 1. When AcA is co-produced in fermentation, EtAc is recovered and the additional unit operations required are presented in Fig. 2. A train of three thermally integrated evaporators is used to concentrate SA fermentation broth. As a result of evaporation, succinate and acetate salts precipitate and are removed by centrifugation. It is assumed that dry solids are obtained, and saturated liquor is recycled to the last evaporation stage.

Dry salts are then mixed with EtOH and H_2SO_4 in two stirred reactors operating in parallel to maintain tank sizes within commercially available dimensions. After dissolution, solid sulfates are removed and the ethanolic solution of acids and esters is sent to the RD unit.

Two inlet streams are fed to the RD unit: the ethanolic acid/ester solution is fed at the top of the reactive zone, and recycled EtOH is fed to the bottom of the reactive zone. In this unit, nearly pure DES is obtained as the bottoms stream, while the EtOH-rich distillate stream also contains H_2O, EtAc, and DEE.

The distillate from the RD unit flows to a subsequent distillation column (C-1) for water removal (Fig. 1), where most of the water is removed in the bottoms and the distillate stream contains less than 10 wt.% water. Even though this distillate stream also contains small amounts of DEE and DES, a ternary diagram including only EtOH, H_2O and EtAc (Fig. S2, Supplementary information) can help to visualize major challenges in further water removal by distillation.

The distillate stream from column C-1 is located close to a distillation boundary (Fig. S2) in a region where only H_2O can be obtained as pure product. Because of the large excess of EtOH in the C-1 distillate, a large amount of highly concentrated EtAc or EtOH (using a recycled stream after further separation) is required to move this stream to a different distillation region where other products can be obtained. In order to avoid excessive use of material and energy, a separation process involving molecular sieves is proposed. In this scenario, most of the water in the C-1 distillate stream is removed and thus the C-1 distillate moves to a region where pure ethanol can be obtained by distillation. As is commonly practiced in the EtOH industry, the molecular sieves are regenerated by recycling around 20% of processed distillate stream into a parallel molecular sieve unit operating in a regeneration cycle. Then regenerating stream is sent back to column C-1 where water adsorbed in the molecular sieves exits in the column bottom stream.

When AcA is not co-produced with SA in fermentation, pure ethanol is obtained from the molecular sieves and can be recycled to reactors or the RD unit. However, a purge stream must be implemented to remove DEE and avoid its buildup in the system. Under these conditions, the purge stream will contain a substantial amount of EtOH.

If AcA is co-produced, then EtAc is present in the C-1 distillate stream in concentrations greater than 20 wt.% (Fig. S2) and must be recovered by further processing. After water removal via molecular sieves, the remainder of the C-1 distillate is in a region where pure EtOH can be obtained as a bottoms product from column C-2 (Fig. 2). In this case, separation is limited by another distillation boundary where the EtOH–EtAc azeotrope is obtained as distillate from C-2. However, as seen in Fig. S3 (Supplementary information), increasing pressure moves the distillation boundary such that the C-2 distillate stream can be separated in column C-3 to obtain pure EtAc as bottom product. The distillate from this final column is recycled to column C-2, but a purge is again required to remove